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Quantitative assessment of worldwide contamination of air, water and soils by trace metals

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Calculated loading rates of trace metals into the three environmental compartments demonstrate that human activities now have major impacts on the global and regional cycles of most of the trace elements. There is significant contamination of freshwater resources and an accelerating accumulation of toxic metals in the human food chain.

THE inventory of emissions from different industrial sources is needed both in global mass balance models for trace metals and also for relating the mesoscale variations in aerosol concentration and composition to global circulation patterns. Estimates of the source strengths are a necessary first step in the design of pollution control programmes, and are also invaluable in the assessment of the long-term ecological and health impacts of the large quantities of toxic metals now being dispersed globally in the different environmental compartments[1]. One of us (J.O.N.) previously presented a global inventory of anthropogenic emissions of Cd, Cu, Ni, Pb and Zn to the atmosphere in 1975 (ref. 2). The present report provides a revision of the earlier data and extends the calculations to many more trace elements. We also present, for the first time, worldwide inventories of industrial/municipal discharges of trace metals into soils and the aquatic ecosystems. The calculations provide some perspective on the problem of toxic metal pollution as a global and regional issue.

Source function

The emission factors for the release of trace elements to the atmosphere are shown in Table 1, and are based on the review of emission studies in Western Europe, the United States, Canada and the Soviet Union[3]. It is known[1] that pollution control strategies in the developing countries are often less stringent than those of Europe and North America. The emission factors used in this report may thus under-represent the global rate of metal emissions.

In most cases, the ranges in the emission factors listed in Table 1 fall within a factor of 2-10. Basically, the range is determined by (1) the concentrations of the trace elements in the raw material; (2) the production technology employed in the emitting industry; and (3) the type and efficiency of the pollution control installations. The concentrations of trace elements in industrial raw material and the associated airborne wastes can obviously vary by more than a factor of 2-10. For example, the As concentrations in coal range from 0.34 to 130 $\mu g\ g^{-1}$ and reach 1,500 $\mu g\ g^{-1}$ in some Czechoslovakian lignites[4]. Such coals with extreme As levels are used locally for domestic purposes and although they can be excluded in deriving the global As emission inventory, they certainly should be considered in estimating the local or even national emissions.

Special attention has been given to deriving the correct emission factors for various production technologies within the same industry. This is particularly true of the high-temperature processes employed in non-ferrous metal smelters (roasting, smelting and refining steps), iron and steel production (electric arc and basic oxygen furnaces versus the older open-hearth plants), and wet versus dry kiln operations in the cement industry. Refuse incineration is becoming a very important source of trace metals in the atmosphere[4]. Because of the large difference in the chemical make-up of the refuse inputs in various countries, it is difficult to select a reasonable range of emission factors for this source and the values used in this study are very tentative. Metal applications in various industries as well as specific uses of certain metals can also emit significant amounts of trace metals; such contributions have been lumped under the miscellaneous heading (Table 2).

Practically every industry discharges one trace metal or the other into the water or soil. We have limited our inventory to the principal industrial and commercial users of water and producers of solid wastes. Extensive data bases currently exist on the trace metal concentrations in industrial and municipal solid wastes and aqueous effluents (for example, see refs 5-19) and the emission factors in Table 3 are based on a critical survey of the published literature. In general, where the reported concentrations appear to be too high, the lower end of the concentration range has been adopted in this report.

The average serviceable lives of the major metal-containing products are unknown. In estimating the loadings into the soils, we have assumed, quite tentatively, that for the metals (namely Mn, Mo, Ni, Sb and V) used primarily in manufacturing durable goods, only 1-5% of their global production is wasted (discarded, applied or washed off due to corrosion) annually on land. For Cd, Cu, Pb Cr and Zn which find significant applications as fertilizer, pigment, lubricant or chemicals, the wastage rate is assumed to be 5-10% of the annual production figure. For Hg (used extensively as pesticide) and Se (widely used as an additive in animal and poultry feeds), the wastage rate is conservatively estimated to be 10-15%. About 80-90% of the As produced each year is applied on soils as agricultural organic pesticides.

It is impossible to place an error range on the calculated inventories. The exact global value of the metal consumed or waste generated are unlikely to differ from those used in this report by more than a factor of two or so; a single number rather than a range in values for the annual global discharge or production/consumption has been employed in this paper. The principal uncertainty in calculating the contribution from each source therefore stems from the wide range in metal concentrations in the discharges. We have endeavoured to use the common ranges in the reported concentrations and unlike most of the previously reported inventories[20-26], we have eschewed the use of an 'average' emission factor in the calculations.

Validation of the global and regional inventories of trace metal emissions published by us has been encouraging. The trace metal profiles (or records) in the Arctic snowfields[2], lake sediments and peats (see ref. 28 for a good overview), and soils[5,29] are in reasonable accord with the calculated historical changes in rates of anthropogenic emissions to the atmosphere[2]. Using a mass balance receptor model, Pacyna *et al.*[30-32] obtained a good fit between the atmospheric concentrations at Ny Alesund, Spitsbergen, and the estimated emissions of trace metals for European sources. Such an agreement between the

Table 1 Emission factors for the release of trace metals to the atmosphere

Source category	Unit	As	Cd	Cr	Cu	Hg	In	Mn	Mo
Coal combustion									
-electric utilities	$\mu g\ MJ^{-1}$	15-100	5-25	80-500	60-200	10-35		70-450	15-150
-industry and domestic	$g\ t^{-1}$	0.2-2.10	0.1-0.5	1.7-12	1.4-5	0.5-3.0		1.5-12	0.4-2.5
Oil combustion									
-electric utilities	$\mu g\ MJ^{-1}$	1.0-5.0	4-30	15-100	60-400			10-100	10-70
-industry and domestic	$g\ t^{-1}$	0.02-0.2	0.05-0.2	1.0-5.0	0.5-3.0			1.0-5.0	0.3-1.5
Pyrometallurgical non-ferrous metal production									
-mining	$g\ t^{-1}$ metal	5.0-10.0	0.1-0.5		20-100			50-100	
-Pb production	$g\ t^{-1}$ metal	200-400	10-50		60-80	2-4.0			
-Cu-Ni production	produced	1,000-1,500	200-400		1,700-3,600		1.0-4.0	100-500	
-Zn-Cd production		50-150	200-1,000		50-150	8-45	0.5-1.0		
Secondary non-ferrous metal production	$g\ t^{-1}$ waste		2.5-4.0		50-150				
Steel and iron manufacturing	$g\ t^{-1}$ steel	0.5-3.5	0.04-0.4	4.0-40.0	0.2-4.0			1.5-40.0	
Refuse incineration									
-municipal	$g\ t^{-1}$ waste	1.1-2.8	0.4-10	0.7-7.0	7.0-14	1.0-15		1.8-9.0	
-sewage sludge		5.0-10	1.0-12	50-150	10-60	5-20		50-100	
Phosphate fertilizers	$g\ t^{-1}$ fertilizer		0.5-2.0		1.0-5.0				
Cement production	$g\ t^{-1}$ cement	0.2-1.0	0.01-0.60	1.0-2.0					
Wood combustion	$g\ t^{-1}$ wood	0.1-0.5	0.1-0.3		1.0-2.0	0.1-0.5			

Source category	Unit	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Coal combustion									
-electric utilities	$\mu g\ MJ^{-1}$	90-600	50-300	10-50	7-50	10-50	10-40	20-300	20-500
-industry and domestic	$g\ t^{-1}$	2.0-15.0	1.0-10.0	0.2-1.5	0.8-2.0	0.1-1.0	0.5-1.0	1.0-10.0	1.5-12.0
Oil combustion									
-electric utilities	$\mu g\ MJ^{-1}$	60-2,500	40-300		6-50	60-400		1,200-9,000	30-220
-industry and domestic	$g\ t^{-1}$	20-80	2.0-6.0		0.3-1.5	0.8-10.0		60-200	1.0-7.0
Pyrometallurgical non-ferrous metal production									
-mining	$g\ t^{-1}$ metal	~100	500-1,000	1.0-10.0	1.0-2.5				50-100
-Pb production	$g\ t^{-1}$ metal	85	3,000-6,000	50-100	10-50				50-120
-Cu-Ni production	produced	900	1,300-2,600	50-200	50-150	50-200		5-10.0	500-1,000
-Zn-Cd production			1,200-2,500	10-20	20-50				100,000-180,000
Secondary non-ferrous metal production	$g\ t^{-1}$ waste		50-800	1-5	1-5				300-1,600
Steel and iron manufacturing	$g\ t^{-1}$ steel	0.05-10.0	1.5-20.0	0.005-0.1	0.001-0.003			0.1-2.0	10-45
Refuse incineration									
-municipal	$g\ t^{-1}$ waste	0.7-3.0	10-20	3.0-6.0	0.2-0.5	1.0-10			20-60
-sewage sludge		10-50	80-100	5-20	1.0-10	5.0-20		3.0-20	50-150
Phosphate fertilizers	$g\ t^{-1}$ fertilizer	1.0-5.0	0.4-2.0		0.003-0.009				10-50
Cement production	$g\ t^{-1}$ cement	0.1-1.0	0.02-16.0				3.0-6.0		2.0-20.0
Wood combustion	$g\ t^{-1}$ wood	1.0-3.0	2.0-5.0						2.0-10.0

A blank space in this table (and Table 2) denotes an insignificant contribution from a particular source.

emission estimates and the trace metal distribution in the environment suggests that the model used in the source inventory does yield data that are of the right order of magnitude.

Atmospheric emissions

The emission factors and the statistics on global production or consumption of industrial goods have been used to calculate the worldwide emissions of trace metals to the atmosphere (Table 2). (A blank in this table implies an insignificant contribution from a particular source.) For most of the trace elements, the calculated total emissions vary by a factor of 2-3; the median values are also shown and may be considered the 'average' rates of global emissions.

Combustion of hard coal, lignites and brown coal in electric power plants and in industrial, commercial and residential burners is the major source of airborne Hg, Mo and Se and a very significant source for As, Cr, Mn, Sb and Tl. Combustion of oil for the same purpose is the most important source of V and Ni and is an important contributor of Sn. The non-ferrous metal industry accounts for the largest fraction of Pb (in addition to gasoline combustion), As, Cd, Cu and Zn emitted. Chromium and Mn are derived primarily from the iron and steel industry (see Table 2).

Our data generally differ from the emission rates that have been reported in the literature. Some of the previous studies have not adequately assessed the important emission sources and the emission factors used have not always considered the differences in industrial processes and pollution control strategies. For example, the emission rates reported by Lantzy and Mackenzie[21] are very different from our estimates. They calculated the industrial emissions on the basis of published chemical composition of metal-enriched, fine-grained aerosols, and estimated the fossil fuel contributions assuming, quite erroneously, that 90% of the metal concentrations in the oil and coal is released to the atmosphere. Their emission rate for lead also excluded the very important automotive contribution.

Previous estimates[23,24,33] of anthropogenic emissions of Hg generally fall in the range 2,000-10,000 tonnes, and are in agreement with our own inventory. The reported As emission rates of 23,600-28,000 tonnes[20,25] fall close to the maximum values in Table 2. The total (volatile+particulate) Se emission of 6,700-8,300 tonnes recently reported by Ross[26] is in good agreement with our own estimate of 3,020-9,625; it is gratifying to note that the Se emission rate of 6,000 tonnes yr^{-1} recently reported by Mosher and Duce[34] is identical to our own estimate (see footnote, Table 2). The inventories for 1975 previously reported by Nriagu[2] were 56,000, 449,000, 470,000 and 314,000 tonnes respectively for Cu, Pb, Ni and Zn. The current (1983/84) emission rates for Cu, Pb and Zn are lower than those of 1975, due mostly to the overall global reduction in the emission of particulates by industries and the phase down in the consumption of leaded gasoline[35]. It seems that the rate for Ni in 1975 was underestimated.

Mean global emissions rates from natural sources have recently been estimated to be (in tonnes per year) 7,800 for As, 1,000 for Cd, 5,400 for Co, 19,000 for Cu, 516,000 for Mn, 26,000

Table 2 Worldwide emissions of trace elements to the atmosphere in 1983 (10^3 kg yr^{-1})

Source category	Global production consumption (10^9 kg yr^{-1})	As	Cd	Cr	Cu	Hg	In	Mn	Mo
Coal combustion									
-electric utilities	[15.5×10^9 MJ]	232-1,550	77-387	1,240-7,750	930-3,100	155-542		1,080-6,980	232-2,320
-industry and domestic	990	198-1,980	99-495	1,680-11,880	1,390-4,950	495-2,970		1,485-11,880	396-2,480
Oil combustion									
-electric utilities	[5.8×10^9 MJ]	5.8-29	23-174	87-580	348-2,320			58-580	58-406
-industry and domestic	358	7.2-72	18-72	358-1,790	179-1,070			358-1,790	107-537
Pyrometallurgical non-ferrous metal production									
-mining*		40.0-80	0.6-3		160-800			415-830	
-Pb production	3.9	780-1,560	39-195		234-312	7.8-16			
-Cu-Ni production	8.5	8,500-12,750	1,700-3,400		14,450-30,600	37-207	8.5-34.0	850-4,250	
-Zn-Cd production	4.6	230-690	920-4,600		230-690		2.3-4.6		
Secondary non-ferrous metal production†			2.3-3.6		55-165			1,065-28,400	
Steel and iron mfg	710‡	355-2,480	28-284	2,840-28,400	142-2,840				
Refuse incineration									
-municipal	140§	154-392	56-1,400	98-980	980-1,960	140-2,100		252-1,260	
-sewage sludge	3‖	15-60	3-36	150-450	30-180	15-60		5,000-10,000	
Phosphate fertilizers	137		68-274		137-685				
Cement production	890	178-890	8.9-534	890-1,780					
Wood combustion	600¶	60-300	60-180		600-1,200	60-300			
Mobile sources	647 (gasoline)								
Miscellaneous		1,250-2,800							
Total, emissions		**12,000-25,630**	**3,100-12,040**	**7,340-53,610**	**19,860-50,870**	**910-6,200**	**11-39**	**10,560-65,970**	**793-5,740**
Median value		18,820	7,570	30,480	35,370	3,560	25	38,270	3,270

Source category	Ni	Pb	Sb	Se	Sn	Tl	V	Zn
Coal combustion								
-electric utilities	1,395-9,300	775-4,650	155-775	108-775	155-755	155-620	310-4,650	1,085-7,750
-industry and domestic	1,980-14,850	990-9,900	198-1,480	792-1,980	99-990	495-990	990-9,900	1,485-11,880
Oil combustion								
-electric utilities	3,640-14,500	232-1,740		35-290	348-2,320		6,960-52,200	174-1,280
-industry and domestic	7,160-28,640	716-2,150		107-537	286-3,580		21,480-71,600	358-2,506
Pyrometallurgical non-ferrous metal production								
-mining*	800	1,700-3,400	18-176	18-176				310-620
-Pb production	331	11,700-31,200	195-390	195-390				195-468
-Cu-Ni production	7,650	11,050-22,100	425-1,700	427-1,280	425-1,700		43-85	4,250-8,500
-Zn-Cd production		5,520-11,500	46-92	92-230				46,000-82,800
Secondary non-ferrous metal production†		90-1,440	3.8-19	3.8-19				270-1,440
Steel and iron mfg	36-7,100	1,065-14,200	3.6-7.1	0.8-2.2			71-1,420	7,100-31,950
Refuse incineration								
-municipal	98-420	1,400-2,800	420-840	28-70	140-1,400			2,800-8,400
-sewage sludge	30-180	240-300	15-60	3-30	15-60		300-2,000	150-450
Phosphate fertilizers	137-685	55-274		0.4-1.2				1,370-6,850
Cement production	89-890	18-14,240				2,670-5,340		1,780-17,800
								1,200-6,000
Wood combustion	600-1,800	1,200-3,000						
Mobile sources		248,030#						
Miscellaneous		3,900-5,100						1,724-4,783
Total, emissions	**24,150-87,150**	**288,700-376,000**	**1,480-6,540**	**1,810-5,780**	**1,470-10,810**	**3,320-6,950**	**30,150-141,860**	**70,250-193,500**
Median Value	55,650	332,350	3,510	3,790**	6,140	5,140	86,000	131,880

* The following primary production figures from the ores were used in the calculations: 8.0×10^9 kg yr^{-1} for Cu, 3.4×10^9 kg yr^{-1} for Pb, 6.2×10^9 kg yr^{-1} for Zn, and 8.3×10^9 kg yr^{-1} for Mn.
† The following secondary production figures were also used: 1.1×10^9 kg yr^{-1} for Cu, 1.8×10^9 kg yr^{-1} for Pb and 0.9×10^9 kg yr^{-1} for Zn.
‡ The value represents the production of crude steel and is used because all emission factors are calculated with reference to the production of one tonne of crude steel.
§ This figure represents 25% of the municipal refuse generated annually (see Table 4 below).
‖ We have assumed that only 10% of the sewage sludge produced is incinerated.
¶ See ref. 13.
\# It has been calculated assuming that 45% of total leaded motor gasoline in the world has 0.15 g a Pb content of l^{-1} and the rest contains 0.40 g l^{-1}. Also it was assumed that Q gasoline = 0.75 kg dm^{-3}.
** This figure is for particulate Se only. Because volatile Se accounts for about 40% of the Se released[20], the total Se emission is estimated to be 6,320 tonnes yr^{-1}.

for Ni, 19,000 for Pb, 66,000 for V, 46,000 for Zn (all from ref. 3) and 6,000 for Hg (ref. 24). The most recent estimate suggests that 6,000-13,000 tonnes of Se are annually released to the atmosphere from natural sources with 60-80% of the total Se emission being of marine biogenic origin[34]. A comparison of these fluxes from natural sources with the anthropogenic emissions in Table 2 leaves no doubt as to the influence of industrial activities on the atmospheric cycle of the trace elements. On average the anthropogenic emissions of As, Cd, Cu, Ni and Zn exceed the inputs of these elements from natural sources by about two-fold or more; in the case of lead, the ratio of anthropogenic to natural emission rates is about 17.

Discharges into water

The main industrial use for water is in the cooling system. We have, however, considered only the generation of contaminated process waters in deriving the inventories in Table 4. The major sources of trace metal pollution in aquatic ecosystems including the ocean are domestic wastewater effluents (especially As, Cr, Cu, Mn and Ni), coal-burning power plants (As, Hg and Se in particular), non-ferrous metals smelters (Cd, Ni, Pb and Se), iron and steel plants (Cr, Mo, Sb and Zn) and the dumping of sewage sludge (As, Mn and Pb). The atmosphere is the major route of Pb entry in natural waters, a fact that has been well documented in the literature[36-38]. The atmosphere also accounts for over 40% of the V loading, a surprising observation in so far as little is currently known about the atmospheric chemistry of this element.

We are not aware of any published inventory pertaining to the global discharges of metal pollution into the aquatic ecosystems; excellent studies on the marine cycle of trace metals are available however[38-40]. We infer from Table 4 that, for most of the trace metals, the annual anthropogenic inputs into the water exceed the quantities emitted to the atmosphere. Although air pollution by toxic metals has been recognized as a matter of concern, the impacts of loading large quantities of toxic metals into the freshwater resources remain to be fully assessed on the global or regional scale.

If it is assumed that only 25% of the industrial effluents are discharged into lakes and rivers (total volume, 1.3×10^{18} l), the

Table 3 Emission factors for the release of trace metals to the soil and water

Source category	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Water (ng l⁻¹)													
Domestic wastewater													
-Central	0.02-0.09	0.002-0.02	0.09-0.4	0.05-0.2	0-0.002	0.2-0.9	0-0.03	0.1-0.6	0.01-0.06	0-0.03	0-0.05	0-0.3	0.1-0.5
-Non-central	0.02-0.12	0.005-0.02	0.1-0.7	0.07-0.5	0-0.007	0.5-1.5	0-0.03	0.2-0.8	0.01-0.08	0-0.03	0-0.05	0-0.3	0.1-0.6
Steam electric	0.4-0.12	0.001-0.04	0.5-1.4	0.6-3.8	0-0.6	0.8-3.0	0.01-0.2	0.5-3.0	0.04-0.2	0-0.06	1.0-5.0	0-0.1	1.0-5.0
Base metal mining and dressing	0.04-1.5	0.001-0.6	0.008-1.4	0.2-18	0-0.3	1.5-23	0.005-1.1	0.02-1.0	0.5-5.0	0.08-0.7	0.5-5.0	0-0.02	0.04-12
Smelting and refining													
-Iron & steel						2.0-5.2			0.2-0.4				0.8-3.5
-Non-ferrous metals	0.5-6.4	0.004-1.8	1.5-10	1.2-8.5	0.001-0.002	1.0-7.5	0.003-0.2	1.0-12	0.5-3.0	0.04-3.8	1.5-10	0-0.6	1.0-10
Manufacturing processes													
-Metals	0.01-0.06	0.02-0.07	0.6-2.3	0.4-1.5	0-0.03	0.1-0.8	0.02-0.2	0.008-0.3	0.1-0.9	0.1-0.6	0-0.2	0-0.03	1.0-5.5
-Chemicals	0.12-3.4	0.02-0.5	0.5-4.8	0.2-3.6	0.004-0.3	0.4-3.0	0-0.6	0.2-1.2	0.08-0.6	0.004-0.5	0-0.07	0.04-1.0	
-Pulp and paper	0-0.3	—	0.004-0.5	0.01-0.13	—	0.01-015	—	0.02-0.04	0.004-0.3	0.001-0.09	0.002-0.3	—	0.03-0.5
-Petroleum products	0.002-0.2	0-0.04	0.001-0.7	0.002-0.2	0-0.08	—	—	0.004-0.2	0.003-0.4	—	0.002-0.3	—	0.01-0.8
Soils (μg g⁻¹)													
Agric. & food wastes	0-0.4	0-0.2	0.3-6.0	0.2-2.5	0-0.1	1.0-7.5	0.6-2.0	0.4-3.0	0.1-1.8	0-0.6	0-0.5	0.2-1.5	0.8-10
Animal wastes, manure	0.6-2.2	0.1-0.6	5.0-30	7.0-40	0-0.1	25-70	2-12	1.5-18	1.6-10	0-0.43	0.2-0.7	1.0-5.5	75-160
Logging and other wood wastes	0-0.3	0-0.6	0.2-1.6	0.3-4.7	0-0.2	1.6-9.5	0-0.3	0.2-2.1	0.6-7.5	0-0.5	0-0.3	0.1-0.9	1.2-15
Urban refuse	0.2-1.6	2.0-17	15-75	30-90	0-0.6	55-320	0.5-10	5.0-23	40-150	0.3-5.0	0.1-1.5	0.2-1.2	80-220
Municipal sewage sludge	0.3-12	1.0-20	6-550	240-1,030	0.5-9.0	220-540	4.0-16	25-110	140-480	2.1-10	0.3-6.9	11-73	900-2,800
Miscellaneous organic wastes including excreta	0-0.25	0-0.06	0.04-2.3	0.2-2.9	0-0.02	0.4-3.0	0.3-1.9	0.8-15	0.08-7.6	0-0.5	0-0.4	0.5-3.6	0.6-10
Solid wastes, metal mfg	0.03-0.6	0-0.2	1.7-6.3	2.5-20	0-0.1	1.1-13	0.03-0.4	2.2-6.5	11-28	0-0.4	0.03-0.5	0.1-0.6	7.0-50
Coal fly ash and bottom ash†	1.8-10	0.4-3.6	40-120	25-90	0.1-1.3	134-445	4.1-20	15-75	12-65	0.7-6.0	1.1-16	3.0-18	30-130
Fertilizer	0-0.1	0.2-15	0.2-2.3	0.3-3.5	0-0.02	0.8-5.0	0-0.1	1.2-3.3	2.5-14	0-0.03	0.1-0.6	0.2-0.8	1.6-6.5
Peat (agricultural and fuel uses)	0.1-1.3	0-0.3	0.1-0.5	0.4-5.2	0-0.05	14-45	0.4-2.0	0.6-9.4	1.2-6.8	0.1-1.2	0-1.1	0.2-4.5	0.4-9.4

* The emission factors shown, which correspond to the common concentrations of trace metals in the solid wastes or liquid effluents have been compiled from a wide variety of sources including refs 5-19

† The concentrations given are for the coal rather than for fly ash or bottom ash

average concentrations in these waters (based on 25% of the median values in Table 4) would be increased by about 90 ng l^{-1} for Hg, 180 ng l^{-1} for Cd, 800 ng l^{-1} for Se and As, 2,200 ng l^{-1} for Cu and Ni, ~2,500 ng l^{-1} for Zn and over 4,000 ng l^{-1} for Pb. The background concentrations of trace metals in unpolluted lakes and rivers (see refs 41-43 for example) are, in general, several-fold lower than these expected increases. In other words, the current rate of worldwide industrial inputs greatly exceed the baseline burdens of trace metals in the average lake and river. Most of the effluent discharges occur in Europe, North America and some Asian countries, implying that the contamination of the freshwater resources in these regions may be much more severe than is generally realized. This problem has not elicited much discussion because (1) the available data bases are often inadequate for assessing the degree of metal contamination of many lakes and rivers, and (2) the short half lives of trace metals (due to their rapid transfer to the sediments) tend to reduce the concentrations of pollutant metals in the water column[44].

Discharges into the soil

Our inventory (Table 5) clearly suggests that soils are receiving large quantities of trace metals from a wide variety of industrial wastes. The two principal sources of trace metals in soils, however, are the disposal of ash residues from coal combustion and the general wastage of commercial products on land. Urban refuse represents an important source of Cu, Hg, Pb and Zn with notable contributions of Cd, Pb and V also coming via the atmosphere. The large volumes of wastes associated with animal husbandry, logging as well as agricultural and food production can affect the trace metal budget of many soils significantly (Table 5). Although municipal sewage sludge may not be a particularly important source on a global scale, its trace metal content is often so high that it is sometimes unsuitable for disposal on land. On a local scale, municipal sewage represents one of the most important sources of metal contamination in soils.

If the total metal inputs were dispered uniformly over the

Table 4 Anthropogenic inputs of trace metals into the aquatic ecosystems (10^6 kg yr^{-1})

Source category	Annual global discharge* (10^9 m^3)	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Domestic wastewater†														
-Central	90	1.8-8.1	0.18-1.8	8.1-36	4.5-18	0-0.18	18-81	0-2.7	9.0-54	0.9-7.2	0-2.7	0-4.5	0-2.7	9.0-45
-Non-central	60	1.2-7.2	0.3-1.2	6.0-42	4.2-30	0-0.42	30-90	0-1.8	12-48	0.6-4.8	0-1.8	0-3.0	0-1.8	6.0-36
Steam electric	6	2.4-14	0.01-0.24	3.0-8.4	3.6-23	0-3.6	4.8-18	0.1-1.2	3.0-18	0.24-1.2	0-0.36	6.0-30	0-0.6	6.0-30
Base metal mining and dressing	0.5	0-0.75	0-0.3	0-0.7	0.1 9	0-0.15	0.8-12	0-0.6	0.01-0.5	0.25-2.5	0.04-0.35	0.25-1.0	—	0.02-6
Smelting and refining														
-Iron and steel	7						14-36			1.4-2.8				5.6-24
-Non-ferrous metals	2	1.0-13	0.01-3.6	3-20	2.4-17	0-0.04	2.0-15	0.01-0.4	2.0-24	1.0-6.0	0.08-7.2	3.0-20	0-1.2	2.0-20
Manufacturing processes														
-Metals	25	0.25-1.5	0.5-1.8	15-58	10-38	0-0.75	2.5-20	0.5-5.0	0.2-7.5	2.5-22	2.8-15	0-5.0	0-0.75	25-138
-Chemicals	5	0.6-7.0	0.1-2.5	2.5-24	1.0-18	0.02-1.5	2.0-15	0-3.0	1.0-6.0	0.4-3.0	0.1-0.4	0.02-2.5	0-0.35	0.2-5.0
-Pulp and paper	3	0.36-4.2	—	0.01-1.5	0.03-0.39	—	0.03-1.5	—	0-0.12	0.01-0.9	0-0.27	0.01-0.9	—	0.09-1.5
-Petroleum products	0.3	0-0.06	—	0-0.21	0-0.06	0-0.02	—	—	0-0.06	0-0.12	0-0.03	0-0.09	—	0-0.24
Atmospheric fallout‡		3.6-7.7	0.9-3.6	2.2-16	6.0-15	0.22-1.8	3.2-20	0.2-1.7	4.6-16	87-113	0.44-1.7	0.54-1.1	1.4-9.1	21-56
Dumping of sewage sludge§	(6×10^9 kg)	0.4-6.7	0.08-1.3	5.8-32	2.9-22	0.01-0.31	32-1.06	0.98-4.6	1.3-20	2.9-16	0.18-2.9	0.26-3.8	0.72-4.3	2.6-31
Total input, water		**12-70**	**2.1-17**	**45-239**	**35-90**	**0.3-8.8**	**109-414**	**1.8-21**	**33-194**	**97-180**	**3.9-33**	**10-72**	**2.1-21**	**77-375**
Median value		**41**	**9.4**	**142**	**112**	**4.6**	**262**	**11**	**113**	**138**	**18**	**41**	**12**	**226**

* The discharges given represent contaminated process waters, and do not include cooling waters.

† The wastewater production figure corresponds to about 60 m^3 $capita^{-1}$ yr^{-1} multiplied by the 2.4×10^9 residents in urbanc and rural areas of the world. The other discharge figures likewise have been derived from the reported water demand per unit tonne of metal smelted or goods manufactured.

‡ We have assumed that 70% of each metal emitted to the atmosphere is deposited on land and the remaining 30% in the aquatic environments[23,29].

§ Worldwide sewage sludge production is estimated to be 30 million tonnes, assuming average sludge production rate of 30 g $capita^{-1}$ day^{-1} in urban and rural communities[8,10]. It is believed that 20% of the municipal sludge is directly discharged or dumped into aquatic ecosystems, about 10% is incinerated and the rest is deposited on land.

Table 8 Worldwide emissions of trace metals into soils (10^6 kg yr^{-1})*

Source category	Annual global discharge ($\times10^{12}$ kg)	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Agric. and food wastes	15†	0-6.0	0-3.0	4.5-90	3-38	0-1.5	15-112	9-30	[illegible]	1.5-27	0-9	0-7.5	3-22	12-150
Animal wastes, manure	2‡	1.2-4.4	0.2-1.2	10-60	14-80	0-0.2	50-140	4-24	3-36	3.2-20	0-0.8	0.4-1.4	2-11	150-320
Logging & other wood wastes	11†	0-3.3	0-2.2	2.2-18	3.3-52	0-2.2	18-104	0-3.3	2.2-23	6.6-8.2	0-5.5	0-3.3	1.1-9.9	13-65
Urban refuse	440§	0.09-0.7	0.88-7.5	6.6-33	13-40	0-0.26	7.0-42	0.22-4.4	2.2-10	18-62	0.22-1.3	0.04-0.62	0-0.4	22-97
Municipal sewage sludge	20‖	0.01-0.24	0.02-0.34	1.4-11	4.9-21	0.01-0.8	4.4-11	0.08-0.32	5.0-22	2.8-9.7	0.04-0.2	0.01-0.14	0.22-1.5	18-57
Miscellaneous organic wastes including excreta	210¶	0-0.25	0-0.01	0-0.1-0.48	0.04-0.61	—	0.08-0.63	0.06-0.4	0.17-3.2	0.02-1.6	0-0.11	0-0.08	0.11-0.76	0.13-2.1
Solid wastes, metal mfg.	380#	0.01-0.21	0-0.08	0.65-2.4	0.95-7.6	0-0.08	0.41-4.9	0-0.16	0.84-2.5	4.1-11	0-0.16	0-0.19	0.03-0.22	2.7-19
Coal fly ash and bottom fly ash	3,720**	6.7-37	1.5-13	149-446	93-335	0.37-4.8	498-1,655	15-74	56-279	45-242	2.6-22	4.1-60	11-67	112-484
Fertilizer	166	0-0.02	0.03-0.25	0.03-0.38	0.05-0.58	—	0.13-0.83	0-0.02	0.20-0.55	0.42-2.3	—	0.02-0.10	0.03-0.13	0.26-1.1
Peat (agricultural and fuel uses)	375††	0.04-0.5	0-0.11	0.04-0.19	0.15-2.0	0-0.02	5.2-17	0.15-0.75	0.22-3.5	0.45-2.6	0.04-0.45	0-0.41	0.08-1.7	0.15-3.5
Wastage of commercial products‡‡		36-41	0.78-1.6	305-610	395-790	0.55-0.82	100-500	0.65-3.2	6.5-32	195-390	0.8-4.0	0.1-0.2	0.6-2.6	310-620
Atmospheric fallout§§ (k)		8.4-18	2.2-8.4	5.1-38	14-36	0.63-4.3	7.4-46	0.55-4.0	11-37	202-263	1.0-3.9	1.3-2.6	3.2-21	49-135
Total input, soils		**52-112**	**5.6-38**	**484-1,309**	**541-1,367**	**1.6-15**	**706-2,633**	**30-145**	**106-544**	**479-1,113**	**4.7-47**	**6.0-76**	**43-222**	**689-2,054**
Median value		82	22	896	954	8.3	1,670	[illegible]	325	[illegible]	26	41	132	1,372
Mine tailings‖‖ (l)		7.2-11	2.7-4.1	—	262-787	0.55-2.8	—	2.1-16	22-64	130-390	16-24	0.28-0.41	1.9-14	194-620
Smelter slags and wastes¶¶ (m)		4.5-9.0	1.6-3.2	—	395-790	0.05-0.28	—	3.2-6.5	32-65	195-390	8-16	0.1-0.2	2.8-6.0	310-620
Total discharge on land		64-132	9.9-45	—	1,198-2,944	2.2-18	—	35-168	160-673	806-1,893	29-87	6.4-77	45-242	1,193-3,294

* The emission figures are derived from the global waste discharges and the estimated emission factors given in Table 2.
† Derived from ref. 45.
‡ This corresponds roughly to the quantity of plants eaten by domestic animals[45].
§ It is assumed that each urban resident generates 660 g refuse per day[18] and that 25% of all the urban refuse is incinerated.
‖ Worldwide sewage sludge production is estimated to be 30 million tonnes, assuming average sludge production rate of 30 g per capita^{-1} per day in urban and rural communities[[illegible],19]. It is believed that 20% of the municipal sludge is directly discharged or dumped into aquatic ecosystems, about 10% is incinerated and the rest (70%) is disposed of on land.
¶ This figure represents waste production in non-urban areas equivalent to about 25 g capita^{-1} day^{-1}.
\# Assuming that each kg of metal processes or fabricated yields 0.5 kg of slag and waste.
** We have assumed that 75% of each of the trace metals present in coal[10-12] is retained in the 'ashes'. The annual coal production figure is from *Encyclopedia Britannica Ann. Suppl.* 1987.
†† About 305×10^6 tonnes of peat are used for agriculture and 69×10^6 tonnes used for fuel. We have assumed that 75% of the trace metals in the peat burned are retained in the ashes.
‡‡ We have proposed that 1-15% of the total annual production of the metals may be discarded (lost due to corrosion for instance), or dispersed in soils from usage as chemicals, pesticides, crop preservatives, etc. (see text). The production figures used (in million tonnes) are: Cd = 0.014, As_2O_3 = 0.06, Cr (chromite) = 8.9, Sb = 0.08, Co = 0.024, Cu = 7.9, raw steel = 710, Pb = 3.9, Mn = 9.6, Hg = 0.0055, Mo = 0.063, Ni = 0.65; phosphate rock = 137, Se = 0.0014, V = 0.058, Zn = 6.2 (ref. 48).
§§ From Table 2, and the assumption specified in footnote (‡) of the same table.
‖‖ We have assumed the average tenor for Pb, Cu, Ni and Zn ore to be 2-6%, and that the tailings contain 0.2% of each of these elements. For Mo and V, the ore tenor is assumed to be 0.2-1.5% and the tailings are left with 0.05% of each element. Typical ore tenor for Hg is 0.1-0.5%, and the tailings are assumed to contain 0.02% Hg. For Cd, As, Sb and Se obtained primarily as by-products associated with base metals, it is assumed that 20-30% of each metal content of the ores are left in the tailings.
¶¶ The retention in smelter slags is estimated to be 1-5% of the Hg produced, 5-10% of the Pb, Cu, Ni, Zn, Mo and V, and 10-20% of the As, Cd, Sb and Se produced.

cultivated land area of 16×10^{12} m^2 (ref. 45), the annual rates of metal application would vary from about 1.0 g ha^{-1} for Cd and Sb to about 50 g ha^{-1} for Pb, Cu and Cr to over 65 g ha^{-1} for Zn and Mn. Although discernable increases have been noted in the metal burdens of some surface soils[29,46], the large background reservoir of trace metals generally obscures such huge loadings from industrial sources. Nevertheless, each soil has a limited retention capacity for trace metals and there is growing concern that many soils in Japan and central Europe either have become or will soon become overloaded with toxic metals at the current rate of anthropogenic input[29,46,47]. The technology for decontaminating such soils has yet to developed.

Conclusions

The inventories presented here clearly show that mankind has become the most important element in the global biogeochemical cycling of the trace metals. The man-induced mobilization of trace metals into the biosphere (median values in thousand tonnes yr^{-1} of the terrestrial plus aquatic inputs minus atmospheric emissions) comes to about 120 for As, 30 for Cd, 2,150 for Cu, 11 for Hg, 110 for Mo, 470 for Ni, 1,160 for Pb, 72 for Sb, 79 for Se, 71 for V, and 2,340 for Zn. The annual total toxicity of all the metals mobilized, in fact, exceeds the combined total toxicity of all the radioactive and organic wastes generated each year, as measured by the quantity of water needed to dilute such wastes to drinking water standard. Each year, millions of tonnes of 'new' trace metals are produced from the mines and subsequently redistributed in the biosphere. The greatly increased circulation of toxic metals through the soils, water and air and their inevitable transfer to the human food chain remains an important environmental issue which entails some unknown health risks for future generations.

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